



EX-SITU PREPARED NAFION-IONIC LIQUID COATED MERCURY FILM ELECTRODE FOR ADSORPTIVE STRIPPING VOLTAMMETRY OF LEAD IN THE PRESENCE OF AMARANTH

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ABSTRACT

Nafion and the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM]F₃MSO₃) coated on a mercury film electrode (NILHgFE) allow us to determine Pb(II) by adsorptive stripping voltammetry in the presence of Amaranth (Am). The NILHgFE was characterized by square wave voltammetry without and in the presence of different ionic liquids obtaining higher peak current with [EMIM]F₃MSO₃ (2.5 mol L⁻¹) compared with other ionic liquids with smaller anions. Optimal analytical conditions were found to be: pH = 2.6 (BR buffer); C_{Am} = 0.77 μmol L⁻¹; E_{ads} = -0.30 V and t_{ads} = 80 s. The Pb-Am complex is reduced at -0.51 V. Peak current is proportional to Pb concentration over the 0.9–10.0 μg L⁻¹ range, with a 3σ detection limit of 0.4 μg L⁻¹. The relative standard deviation for a Pb solution (4.9 μg L⁻¹) was 2.0 % for seven successive assays. The method was validated by determining Pb(II) in certified reference wastewater (SPS-WW1). Finally, the method was applied to the determination of Pb(II) in tap water samples after UV digestion with satisfactory results.

Indexing terms/Keywords

Adsorptive stripping voltammetry; Nafion-Ionic Liquid-coated mercury film electrode; Pb(II) determination; Amaranth.

Academic Discipline And Sub-Disciplines

Chemistry; Analytical Chemistry; Electroanalytical Chemistry.

SUBJECT CLASSIFICATION

Quantitative analysis

TYPE (METHOD/APPROACH)

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1. INTRODUCTION

The development the new sensitive methods for the monitoring of Pb(II) in natural waters is of great importance for ecological assessments, due to the fact that this toxic element tend to concentrate in all aquatic environmental matrices and is taken up by marine species that form part of the human food chain causing different diseases and some type of cancer [1,2]. Electroanalytical techniques have important advantages including speed of analysis, high selectivity and sensitivity, low detection limit, relative simplicity and low cost of equipment compared to atomic absorption and emission spectrophotometric techniques [3]. Among of these, stripping voltammetry is the most sensitivity because it has a preconcentration step on the electrode surface prior to getting the voltammogram. Traditionally, the hanging mercury drop electrode (HMDE), due to its sensitivity has been used most widely as the working electrode for Pb determination [1,4–7]. In the last years, modified electrodes consisting of a thin metallic film electroplated on an inert substrate coating of different permselective membrane materials have been introduced. The Dupont company was the first to develop a chemically inert and electroinactive copolymer derived from tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether containing strongly acidic $\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ terminal groups that was given the trade name Nafion [8–10,11]. On the other hand, ionic liquid carrying long-chain alkyl groups as 1-butyl-3-methylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium ethylsulfate interact with the electrode increasing electron transference rate and the peak current of Pb [12–14]. The large majority of the published applications on the determination of Pb using different electrodes have utilized anodic stripping voltammetry (ASV). Adsorptive stripping voltammetry (AdSV) involves the formation, adsorptive accumulation and then reduction of a surface-active complex of the metal. The ligands used must be good complexing agents, in addition to contain $-\text{OH}$, $-\text{SH}$ or other groups with unpaired electrons to interact with the working electrode and adequate charge. Some ligands used in adsorptive stripping voltammetry of lead are: carbidopa [15], 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt (SPADNS) [4], 2-acetylpyridine salicyloylhydrazone (2-APSH) [16], 2-hydroxybenzaldehyde benzoylhydrazone (2-HBBH) [17], dopamine [18] 2-mercaptobenzothiazole [19] and others.

The present paper describes an adsorptive stripping procedure for lead determination in natural waters using amaranth (Am) (trisodium (4E)-3-oxo-4-[(4-sulfonato-1-naphthyl)hydrazono]naphthalene-2,7-disulfonate) as complexing and adsorbing agent. The electrochemical study of amaranth has already been reported [20], to the best of our knowledge there is no literature about the determination of Pb in the presence of this ligand and neither the effect of ionic liquid in the sensibility of the method.

2. EXPERIMENTAL PART

2.1. Apparatus

The voltammograms were obtained on a BASi CV50W in a three-electrode configuration. The modified glassy carbon electrode (NILHgFE, disc diameter of 3 mm), was used as working electrode with a 3 mol L^{-1} $\text{Ag}/\text{AgCl}/\text{KCl}$ reference electrode, and a platinum wire auxiliary electrode. The pH measurements were carried out with an Orion-430 digital pH/mV meter equipped with combined pH glass electrode. UV-irradiation of water samples was carried out in quartz tubes using a 705 UV-digester (Metrohm).

2.2. Reagents and solutions

All the chemicals (nitric acid, ethanol etc.) were analytical grade from Merck (Darmstadt, Germany). Standard Pb(II) and Hg(II) solutions were prepared by diluting commercial standards containing 1000 mg L^{-1} , Merck (Darmstadt, Germany). Amaranth (Am) and Nafion (5% solution in a mixture of lower aliphatic alcohols) were purchased from Sigma-Aldrich. Ionic liquids: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($[\text{EMIM}]\text{F}_3\text{MSO}_3$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}]\text{BF}_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}]\text{PF}_6$) and 1-butyl-3-methylimidazolium tris(pentafluorethyl)trifluorophosphate ($[\text{BMIM}]\text{FAP}$) high purity were purchased from Merck. Britton Robinson (BR) buffer solutions were used to investigate pH. These buffers (0.4 mol L^{-1}) were prepared by mixing equal volumes of orthophosphoric acid, acetic acid, and boric acid, adjusting to the required pH with 2.0 mol L^{-1} NaOH solution. Certified reference water (TMDA-61. Environment Canada), and certified waste water level 1 (SPS-WW1, Norway) were used for validation measurements. All solutions were prepared with high purity water obtained in a Milli-Q system (18.2 M Ω . Millipore, USA).

2.3. Procedure for preparation of NILHgFE

Before measurement, the glassy carbon substrate electrode was thoroughly polished using a polishing pad with 0.3 and 0.05 μm Al_2O_3 slurry, rinsed with 0.3 mol L^{-1} HNO_3 , water and methanol for five minutes in an ultrasonic bath and dried with N_2 . N- $[\text{EMIM}]\text{F}_3\text{MSO}_3$, N- $[\text{BMIM}]\text{BF}_4$, N- $[\text{BMIM}]\text{PF}_6$ and N- $[\text{BMIM}]\text{FAP}$ composites were prepared by mixing 100 μL of 5% Nafion solution with 100 μL of ionic liquids and sonicated por five minutes. 10- μL of nafion solution or 10- μL of nafion-ionic liquid solution was placed on the electrode surface and the solvents were evaporated off at room temperature for 60 min. The electrode was then transferred into the plating solution containing 200 mg L^{-1} Hg(II) and the Hg film was formed by holding the working electrode potential at -1.30 V for 150 s [12]. The same electrode was used in a series of measurements. The electrode modified only with Nafion (NE) and Nafion mercury film (NHgFE) were prepare as was described above but without ionic liquid.



2.4. Sample preparation

Domestic tap water samples were collected in our laboratory. Before the analysis all the samples were digested under UV radiation for 90 min at 90 °C in the presence of H₂O₂ (10.0 mL of sample with 100 µL of 30 % H₂O₂) to decompose organic substances. To make sure of the reliability of the method the samples were analyzed by ICP–AES.

2.5. Measurement Procedure

Ten mL of deionized water (or tap water samples), 0.2 mL of Britton–Robinson buffer (0.4 mol L^{−1}), 1.0–100 µL of amaranth solution (0.50 mmol L^{−1}), and aliquots of Pb(II) solution (1.0 mg L^{−1}) were pipetted into the voltammetric cell. The solution was purged with nitrogen for 300 s in the first cycle and for 60 s for each successive cycle. Then, initiate the preconcentration step for a given t_{ads} and E_{ads} at a stirring speed of 500 rpm. After an equilibration time of 10 s, the adsorptive voltammogram was recorded, while the potential was scanned from −0.10 to −0.90 V using square wave modulation. The parameters as step amplitude, pulse amplitude, and a frequency were investigated. Each voltammogram was repeated three times. The calibration curves were obtained and linear regression and detection limits were calculated. The proposed method was applied to the determination of lead in tap water; in order to eliminate matrix effects the standard addition method was used. All data were obtained at room temperature (~25 °C).

3. RESULTS AND DISCUSSION

3.1. Effect of operational parameters

3.1.1. Characterization of the NILHgFE

Figure 1 shows adsorptive voltammograms of Pb(II) (4.9 µg L^{−1}) in the presence of amaranth (0.2 µmol L^{−1}) in BR buffer pH 2.0, using a nafion coated glassy carbon electrode (curve a), nafion coated mercury film electrode (curve b) and ionic liquid–nafion coated mercury film electrode (curve c). No signal of Pb–Am was observed with nafion coated glassy carbon electrode (N–E, curve a) and one almost imperceptible signal was observed for Pb(II)–Am complex using a nafion coated mercury film electrode. When the electrode was coated with a mixture of nafion and EMIM]F₃MSO₃ (curve c, NILHgFE) the electrochemical reduction of the Pb–Am complex occurred at −0.51 V. The presence of ionic liquid increased the peak current of the complex and the sensitivity of the method was better.

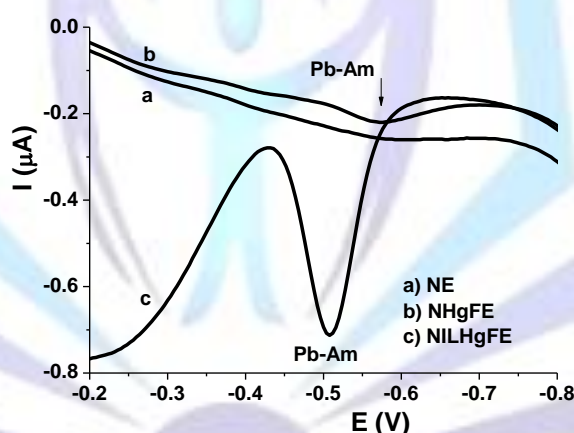


Figure 1. AdSV of Pb(II) (4.9 µg L^{−1}); in the presence of amaranth (0.2 µmol L^{−1}) in BR buffer at pH 2.0 using a nafion coated glassy carbon electrode (NE, curve a), nafion coated mercury film electrode (NHgFE, curve b) and ionic liquid–nafion coated mercury film electrode (EMIM]F₃MSO₃, NILHgFE, curve c). E_{ads} : −0.20 V; t_{ads} : 60 s; pulse amplitude: 25 mV and frequency: 15 Hz.

3.1.2. Study of the influence of ionic liquid types

Comparative study with several ionic liquids with different anion size and different chain size in the organic cation was carried out. The ionic liquid used were: [EMIM]F₃MSO₃ with short–chain and large anion; [BMIM]BF₄ and [BMIM]PF₆ with long–chain and little anion, and [BMIM]FAP with long chain larger anion. All have the same cation. Figure 2 shows the results obtained: no signal was observed for Pb–Am complex when the ionic liquid [BMIM]PF₆ was used (curve b), whereas a poor peak at −0.50 V was observed in the presence of [BMIM]FAP (curve a). This ionic liquids were little soluble in nafion. On the other hand when the ionic liquid [BMIM]BF₄ was added, a signal with high peak current was observed at −0.48 V (curve c), but the highest peak current was obtained with the ionic liquid [EMIM]F₃MSO₃ which presents the highest solubility in nafion and was chosen for this study.

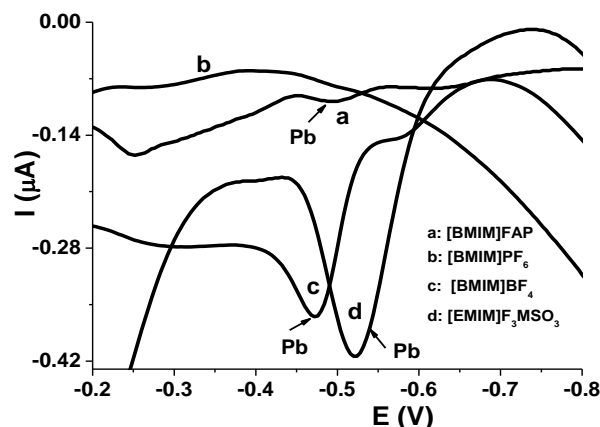


Figure 2. AdSV of Pb(II) ($4.9 \mu\text{g L}^{-1}$); in the presence of amaranth ($0.2 \mu\text{mol L}^{-1}$) in BR buffer at pH 2.0 using a nafion coated mercury film electrode with ionic liquids: [BMIM]FAP (curve a), [BMIM]PF₆ (curve b), [BMIM]BF₄ (curve c) and [EMIM]F₃MSO₃ (curve b). $E_{\text{ads}} -0.20 \text{ V}$, $t_{\text{ads}} 60 \text{ s}$. Other parameters as in Figure 1.

3.1.3. Study of the influence of [EMIM]F₃MSO₃ concentration

The effect of the [EMIM]F₃MSO₃ concentration on the peak current of the Pb–Am complex was investigated in the 0.00 to 5.04 mol L⁻¹ range. As can be observed in Fig.3, the peak current increased with increasing [EMIM]F₃MSO₃ up to 2.5 mol L⁻¹, and then decreased slightly, probably due to saturation of the electrode because the ionic liquid can be strongly adsorbed on electrode surface [21]. An optimum ionic liquid concentration of 2.5 mol L⁻¹ was used for further experiments. These results are similar to the obtain for Pb and Cd with morin as ligand [12].

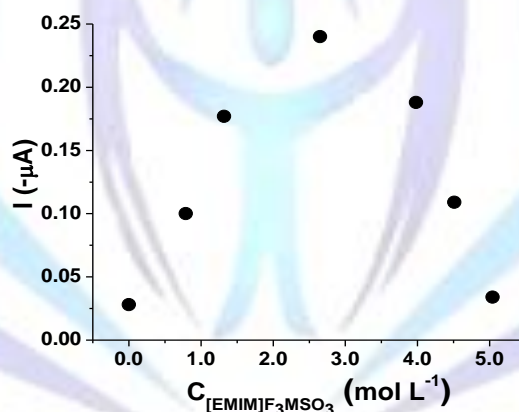


Figure 3. Effect of [EMIM]F₃MSO₃ concentration on the peak current of Pb–Am complex ($4.9 \mu\text{g L}^{-1}$) in the presence of amaranth ($0.2 \mu\text{mol L}^{-1}$) in BR buffer at pH 2.0 using a nafion–ionic liquid coated mercury film electrode (NILHgFE). $E_{\text{ads}} -0.20 \text{ V}$, $t_{\text{ads}} 60 \text{ s}$. Other parameters as in Figure 1.

3.1.4. Effect of pH variation

The influence of pH on the adsorptive peak current of the Pb–Am complex was studied in the 1.8 – 4.8 pH range (Fig. 4). In order to keep the composition of the buffer constant when studying the effect of pH, BR buffers were used. The experimental conditions were: Pb(II): $4.9 \mu\text{g L}^{-1}$; C_{Am} $0.2 \mu\text{mol L}^{-1}$; $E_{\text{ads}} = -0.20 \text{ V}$ and $t_{\text{ads}} = 60 \text{ s}$. It was found that at pH 2.5 the peak current of Pb–Am complex is maximum and then the peak current decreased with increasing pH probably due it changes the net charge of the complexes and the adsorption on the electrode are less effective. Have been reported that the pK_a of amaranth is 3.3.

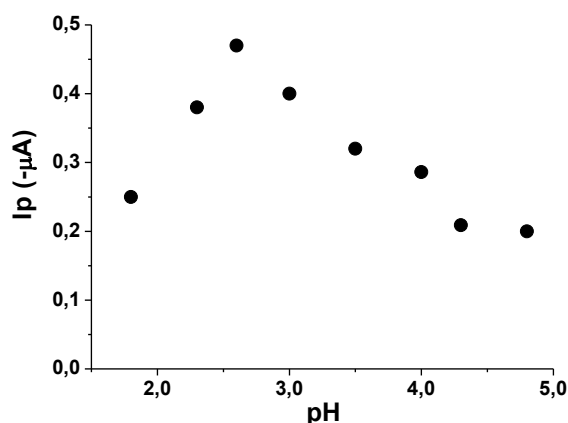


Figure 4. Effect of pH on the peak current of Pb–Am complex ($4.9 \mu g L^{-1}$) in the presence of amaranth ($0.2 \mu mol L^{-1}$). E_{ads} $-0.20 V$, t_{ads} 60 s. Other parameters as in Figure 1.

3.1.5. Effect of Amaranth concentration (C_{Am})

Amaranth ($pK_1 = 3.3$) has good water solubility and forms complexes with Pb(II) of stoichiometry metal:ligand of 1:1. Amaranth concentration had a considerable effect on the method's linear range and sensitivity. The adsorptive signal of Pb in the absence of ligand is not observed. The effect of C_{Am} (range 0.0 to $3.0 \mu mol L^{-1}$) was studied for Pb at concentration level of $4.9 \mu g L^{-1}$ (pH 2.6, BR buffer, $E_{ads} -0.20 V$; t_{ads} 60 s) and it is illustrated in Fig. 5. The peak current increased with increasing C_{Am} up to $0.8 \mu mol L^{-1}$ (M:L ratio of 1:90) and then decreased slightly has probably due to the competition of free amaranth with the Pb–Am complex. An optimum ligand concentration of $0.8 \mu mol L^{-1}$ was used for further experiments.

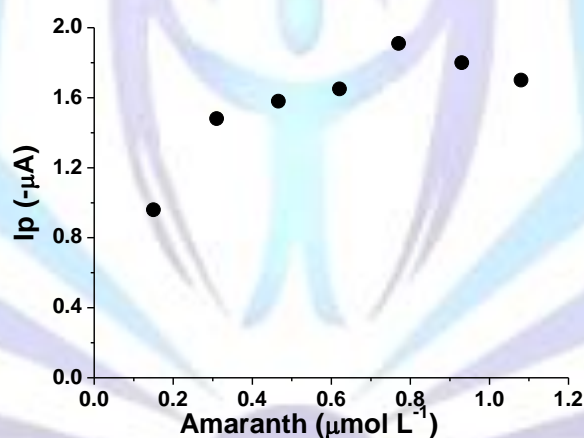


Figure 5. Effect of amaranth concentration on the peak current of Pb–Am complex. Conditions: pH 2.6; Pb(II) $4.9 \mu g L^{-1}$; $E_{ads} -0.20 V$, t_{ads} 60 s. Other parameters as in Figure 1.

3.1.6. Effect of accumulation potential (E_{ads})

Fig. 6 shows the effect of the accumulation potential on the peak current of the Pb–Am complex at pH 2.6 over the 0.1 to $-0.6 V$ range. The experimental conditions were: Pb(II) $4.9 \mu g L^{-1}$; C_{Am} $0.8 \mu mol L^{-1}$ and $t_{ads} = 60 s$. As shown in Fig. 6, the peak current of the Pb–Am complex increased until $-0.30 V$ and then decreased abruptly with more negative potentials. An accumulation potential of $-0.30 V$ gives the best sensitivity and was selected for further measurements.

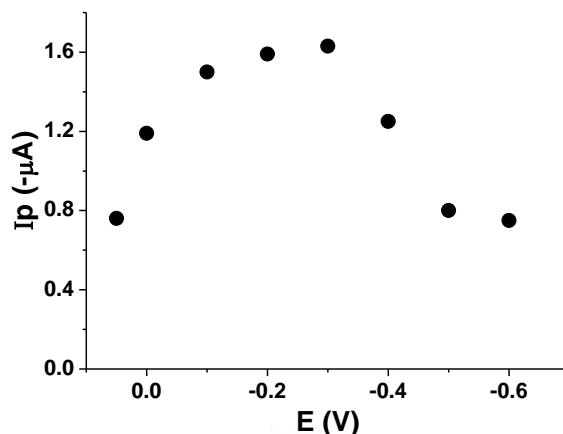


Figure 6. Effect of E_{ads} on the peak current of Pb–Am complex. Conditions: pH 2.6; Pb(II) $4.9 \mu\text{g L}^{-1}$; C_{Am} $0.8 \mu\text{mol L}^{-1}$; t_{ads} 60 s. Other parameters as in Figure 1.

3.1.7. Effect of accumulation time (t_{ads})

The effect of accumulation time was examined in the 10 – 100 s range. The experimental conditions were: pH 2.6; Pb(II) $4.9 \mu\text{g L}^{-1}$; $C_{\text{Am}} = 0.8 \mu\text{mol L}^{-1}$ and $E_{\text{ads}} = -0.30 \text{ V}$. Peak current increases with increasing accumulation time prior to the potential scan, indicating that the amaranth and Pb–Am complex are readily adsorbed on the electrode (Fig. 7). Peak current increased almost linearly with accumulation time until 80 s, and then decreased slightly due to competition with the free ligand for the electrode surface. A t_{ads} of 60 s was used for further studies, but in the analysis of real samples higher times can be used to achieve good sensitivity.

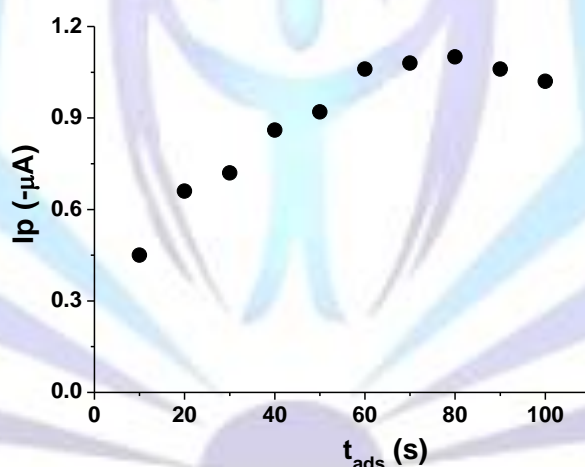


Figure 7. Effect of t_{ads} on the peak current of Pb–Am complex. Conditions: pH 2.6; Pb(II) $4.9 \mu\text{g L}^{-1}$; C_{Am} $0.8 \mu\text{mol L}^{-1}$; $E_{\text{ads}} = -0.30 \text{ V}$. Other parameters as in Figure 1.

3.1.8. Effect of instrumental variables (frequency, step potential and amplitude)

The peak current of the Pb–Am complex increased as the frequency increased from 10 to 30 Hz. However, at frequencies of 30 Hz there was a constant of the peak shape and the background, so 20 Hz was adopted as optimum. Peak current increased linearly with step potential variations from 1 to 10 mV and pulse amplitude from 5 to 20 mV, so 10 mV and 15 mV were adopted as optimum for step potential and pulse amplitude, respectively.



3.2. ANALYTICAL PARAMETERS

3.2.1. Linear range, detection limit, and repeatability of the method

Optimal analytical conditions were found to be a amaranth concentration of $0.8 \mu\text{mol L}^{-1}$, pH 2.6 (BR buffer 0.04 mol L^{-1}), and accumulation potential of -0.30 V . Under these conditions calibration plots were obtained. Peak current is proportional to Pb concentration over the $0.9\text{--}10.0 \mu\text{g L}^{-1}$ range, with a 3σ detection limit of $0.4 \mu\text{g L}^{-1}$. The relative standard deviation for a Pb solution ($4.9 \mu\text{g L}^{-1}$) was 2.0 % for seven successive assays. Fig. 8, show adsorptive voltammograms and calibration plot.

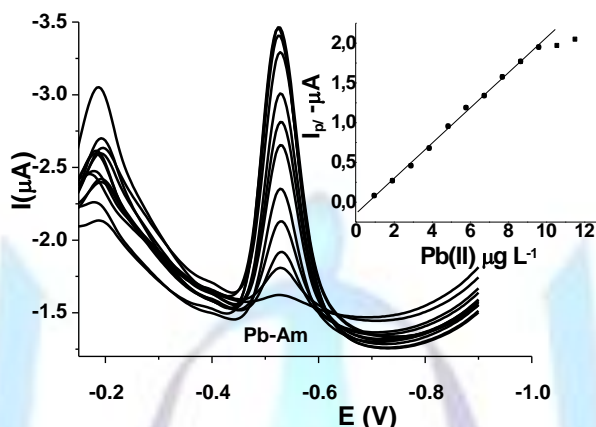


Figure 8. Adsorptive voltammograms and calibration plot of Pb(II) in the presence of amaranth ($0.8 \mu\text{mol L}^{-1}$). Conditions: pH 2.6; E_{ads} : -0.30 V ; t_{ads} : 60 s. Others conditions as in Fig. 1.

3.2.2. Interference studies and validation of the method

The usefulness of the present method was evaluated by determining Pb in certified reference waste water (SPS-WW1) containing Al 2.0; As 0.1; Cd 0.02; Co 0.06; Cr 0.2; Cu 0.4; Fe 1.0; Mn 0.4; Ni 1.0; P 1.0; Pb 0.1; V 0.1 and Zn 0.6 mg L^{-1} . This analysis was carried out with 10.0 mL of deionized water, 1.0 mL of sample, 0.2 mL BR buffer (0.4 mol L^{-1}) and 100 μL of amaranth (0.20 mmol L^{-1}). An optimum amaranth concentration of $0.8 \mu\text{mol L}^{-1}$ was chosen for optimization studies with synthetic solutions. However, when the spiked or real water samples contain several metal ions, a higher ligand concentration ($2.0 \mu\text{mol L}^{-1}$) was used to ensure complete complex formation. Three replicate analyses were performed for each sample. The value obtained for Pb(II) was $9.01 \pm 0.02 \mu\text{g L}^{-1}$ (-9.9% RE) and the plot was also linear until $20.0 \mu\text{g L}^{-1}$.

3.2.3. Analysis of Pb in tap water

The proposed method was applied to the determination of Pb(II) in domestic tap water previously digested with UV radiation in the presence of H_2O_2 solution. These analyses (10-mL samples) were carried out under optimum conditions (pH 2.6; C_{Am} : $2.0 \mu\text{mol L}^{-1}$, t_{ads} : 80 s; E_{ads} : -0.30 V). To check the reliability of the method the samples were analyzed by ICP-AES, however the results obtained with this technique were below $10 \mu\text{g L}^{-1}$, which is the detection limit of this procedure. The value obtained was $5.0 \pm 0.3 \mu\text{g L}^{-1}$ for Pb(II) ($n=5$). The levels are below the limit proposed by the EPA for Pb(II) tap water ($15 \mu\text{g L}^{-1}$).

4. CONCLUSIONS

The coated nafion-ionic liquid coated mercury film electrode; NILHgFE is very suitable for trace analysis of Pb(II) in water samples show highly sensibility and selectivity using $[\text{EMIM}]\text{F}_3\text{MSO}_3$ as ionic liquid. $[\text{BMIM}]\text{BF}_4$ is less sensitive. On the other hand, amaranth is very suitable as adsorbing-complexing ligand for lead determination. Cadmium is not detected with this method.

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Author' biography



Veronica Arancibia PhD is a full professor of Analytical chemistry and a group leader at Catholic University of Chile. Her research interest comprises the optimization of electroanalytical procedures employing different electrodes, their application to the determination of trace metals in environmental, biological and food samples and the effect of external factors (ion pairs, surfactants, ionic liquids, sonoelectrochemistry, etc.) in the sensitivity of the techniques.



Edgar Nagles received his Ph.D. degree from the Catholic University of Chile in 2011. He completed his postdoctoral training on the preparation and development of new structures on electrodes surfaces for improving the determination of heavy metals in natural waters and sediments and the effect of ionic liquids. Actually is auxiliary professor of analytical chemistry in the Amazonia University, Florencia, Colombia.